

Naval Surface Warfare Center

Carderock Division

West Bethesda, Maryland 20817-5700

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October 1997

Survivability, Structures and Materials Directorate
Technical Report

Material Considerations for the Navy Shipboard Waste Destruction System

by

David A. Shifler and Catherine R. Wong

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CONTENTS

LIST OF FIGURES.....	iii
LIST OF TABLES.....	iii
ABSTRACT	1
ADMINISTRATIVE INFORMATION	1
ACKNOWLEDGEMENTS.....	1
INTRODUCTION.....	1
CONCEPT DESIGN	3
Hot Wall Design.....	4
Cold Wall Design	7
Corrosion in High Temperature Environments	11
CONCLUSIONS	18
REFERENCES	20

LIST OF FIGURES

FIGURE 1 - CROSS-SECTION OF REFRACTORY-LINED HOTWALL PAWDS.....	5
FIGURE 2 - COMPARISON OF THICK, CONVENTIONAL REFRACTORY WALL REQUIRED FOR HOTWALL PAWDS DESIGN (LEFT) WITH A LIGHT-WEIGHT, AIR-COOLED COLDWALL DESIGN USING A TBC ON A SUPERALLOY (RIGHT).	9
FIGURE 3 DIAGRAM OF EDUCTOR CONSISTS OF A CENTRAL PLASMA TORCH WHICH WILL PROCESS ORGANIC SHIPBOARD WASTE DRAWN THROUGH THE TUBE AND INTO A SECONDARY CHAMBER.....	9

LIST OF TABLES

TABLE 1- THERMAL DESTRUCTION TECHNOLOGIES ^B	2
TABLE 2 - GREEN BOOK NAVY SOLID WASTE (NSW) GENERATION RATES ^C	3
TABLE 3 - MELTING POINTS OF COMMON REFRACTORIES	4
TABLE 4 - CANDIDATE WORKING REFRACTORIES (2,49)	7
TABLE 5 - CANDIDATE PAWDS ALLOYS - CHEMICAL COMPOSITIONS	10
TABLE 6 - CANDIDATE ALLOY PHYSICAL AND MECHANICAL PROPERTIES	11
TABLE 7 - CORROSION IN VARIOUS HIGH TEMPERATURE ENVIRONMENTS	12

ABSTRACT

Compliance with MARPOL environmental regulations has required the design of a waste management system to reduce the volume of solid shipboard waste and treat it so that it is safe to carry aboard ship. The U.S. Navy in cooperation with industry has developed a conceptual design of a plasma arc waste destruction system (PAWDS) capable of meeting strict shipboard weight, size and operational criteria that has precluded the use of traditional commercial systems. The innovative system design has involved a thorough examination of candidate materials that should be capable of withstanding the processing of a variable waste stream that may include highly corrosive constituents. The structural components of the PAWDS should insure safety to personnel and ship by resisting degradation through high temperature corrosion, erosion, thermal cycling, and other effects.

ADMINISTRATIVE INFORMATION

This work was sponsored by the Naval Sea Systems Command Research, Development, and Standards and the Office of Naval Research, Program Element 060223N, Environmental Quality and Logistics. The program manager of the PAWDS Working Group is Dr. Eugene Nolting, Code 634, of the Environmental Quality Department, Carderock Division, Naval Surface Warfare Center. The work was supervised by Mr. R. J. Ferrara, Code 613 and Dr. L. Aprigliano, Code 612, Carderock Division, Naval Surface Warfare Center.

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INTRODUCTION

U.S. Navy Operational Concept and its strategy "Forward --- From the Sea" requires the Fleet to execute its presence anywhere in the world at any time. Local, national, and international environmental regulations and statutes controlling overboard discharge of liquid and solid wastes and air emissions have become more stringent for ships deployed at sea. The Navy's ability to operate in littoral and selected areas around the world may be compromised unless alternative solid waste management processes are utilized. Existing ships do not have sewage and solid waste holding capabilities to hold wastes for more than a few days.

The International Convention for the Prevention of Pollution from Ships in 1973 and the 1978 Marine Pollution Protocol, collectively known as MARPOL 73/78^A were early initiatives to control waste disposal in the marine environment.

^A MARPOL refers to the International Treaty for the Prevention of Pollution for Ships. The United States is a party to this convention by S. Treaty Document No.3, 100th Congress, 1st Session.

An integrated technology for Navy ships to comply with this solid waste and liquid waste discharge prohibition is not currently available commercially. The marine environment and Naval warfare requirements present significant and unique challenges for technical solutions of waste disposal problems for U.S. Navy ships deployed at sea without significant impact to operations and deployment. Unlike land-based systems, solutions aboard ships will impose considerable constraints on space and must operate reliably in a corrosive, marine environment. The Navy has significant space, weight, reliability, maintainability, and operability constraints which require that any system minimize its impact on ship operations, ship systems, manpower requirements, maintenance, and loss of mission-oriented space.

The Naval Studies Board^B (NSB) has recommended that the Navy continue its program of research into advanced thermal waste destruction technologies that may eventually serve as the principal shipboard waste reduction methodology. A comprehensive survey, as shown in Table 1, of thermal destruction technologies for shipboard solid waste was conducted. The survey identified electrically-heated, plasma-arc pyrolytic thermal destruction technology as the most promising because of its potential for greater reliability, compact size, higher processing temperatures, better temperature control, and greater capacity relative to standard incinerators.

Table 1- Thermal Destruction Technologies^B

Technology	Operational Temperature	Application/ Destruction Characteristics	Gas Products	Solid Products	Waste Reduction	Remarks
Incineration •Starved Air •Excess Air	900 °C 1650 °F	Solids & Liquids by Exothermic Combustion	CO ₂ , H ₂ O, N ₂ Some: Hydrocarbons NO _x , SO ₂	Particulates (Flyash) •Ash •Metal •Glass	High	<u>Low Energy Input</u> Available Units Generally Produce Excessive Air Emissions and Hazardous Ash
Wet Air Oxidation	316 °C 600 °F	Liquids by Low Temperature Pressurized Oxidation	CO ₂ , H ₂ O, Hydrocarbons	Particulate •Char •Inorganics	Moderate	<u>Moderate Energy Input</u> Incomplete Conversion of Organics. Fairly easy to design, build, and control.
Supercritical Water Oxidation	374 °C 705 °F	Liquids by Medium Temperature High Pressure Oxidation	CO ₂ , H ₂ O	Particulates Salts	Maximum	<u>Moderate Energy Input</u> (Depends on Waste Stream) Can Produce Complete Oxidation of Organics.
Plasma Arc •Pyrolysis •Incineration	1500-5000 °C 2700-9000 °F	Solids & Liquids by Very High Temperature/ Gasification Reactions	CO ₂ , H ₂ O, N ₂	Inert Maximum Density Slag	Maximum	<u>Very High Energy Input</u> Air Emissions control is easier with conventional Incineration ash can be vitrified, making it inert.

Ultra-high reaction temperatures derived from plasma energy can achieve waste treatment without combustion. Plasma is produced by passing a gas through a high current electric arc; temperatures within the arc range from 18,000-36,000 °F (10,000-20,000 °C). Temperatures in the outer plume of a plasma flame can range from 5,000 to 11,000°C. This

^B Shipboard Pollution Control, U.S. Navy Compliance with MARPOL Annex V, Committee on shipboard Pollution Control, Naval Studies Board, Commission on Physical Sciences, Mathematics, and Applications, National Research Council, National Academy Press, Washington, DC. p.4 (1996).

combustion-independent plasma heating process allows for extremely high heating rates which can translate into practical reactor configurations having small destruction volumes, high processing rates, short residence times and high destruction efficiencies. A PAWDS can rapidly change the physical and chemical nature of shipboard waste materials. Plasma energy can change organic wastes to their elemental constituents while inorganic solid wastes produce fly ash and a pool of liquefied inorganic-metallic material. The environment in a plasma destruction chamber may be either oxidizing or reducing; the choice of either environment can affect the material selection for the chamber.

CONCEPT DESIGN

Among the many issues involved, the reliability and design of the final PAWDS will be dependent on the materials of construction. One of the primary operational factors, the focus of this paper, is the corrosion resistance of candidate materials; the discussion of many of the other issues is beyond the scope of this paper. Complex processes occur in incineration of solid wastes which involve thermal and chemical reactions that occur at various times, temperatures, and locations. Pyrolysis via high reaction temperatures derived from plasma energy will also encompass complex reactions, dynamic gas flows, particulate and deposition effects, mechanical and chemical mixing, and residence times of the reaction species. The operational mode, the temperatures existing within the primary combustion chamber eductor, secondary combustion, and other system components, composition of the waste stream, the chamber chemical environment, the waste stream abrasiveness, the aforementioned space constraints, safety, maintainability, and reliability will affect the choice of construction materials. The amount of Navy Solid Waste (NSW)^C generated on average (Table 2) has been studied, but the waste stream at any given time is variable. The composition of the ship solid and liquid waste generated on warships at sea can depend in part, on ship size and class, type of mission, length of ship's mission, and location of deployment.

Table 2 - Green Book Navy Solid Waste (NSW) Generation Rates^C

Average Generation Rates		
Waste Stream Constituents	lb/man/day	Weight %
Paper/Cardboard	1.11	35.35
Food	1.28	40.76
Metal	0.41	13.06
Glass	0.13	4.14
Plastic*	0.21	6.69
Total	3.14	100.00

* Note: Plastics are not planned to be processed by PAWDS

Several designs have been considered based on different operating scenarios and different materials. They are: (1) hot wall (refractory lined, minimal cooling), (2) air-cooled cold wall, and (3) water-cooled cold wall.

Hot Wall Design

The first design concept considered for the PAWDS was a refractory-lined, hotwall primary chamber (Figure 1) which would have an approximate service wall temperature of about 1500 °C. The use of a plasma arc would produce a plasma plume temperature of about 5300 °C near the outer plume envelope. Most alloys will degrade in environments with prolonged service temperatures above 1000 °C. Refractories can exist at higher temperatures. Refractories are mainly high-melting point metallic oxides, but also include substances such as carbides, borides, nitrides, and graphite (Table 3). Maximum service temperatures will always be less than the melting points of pure ceramics because refractories usually contain minor constituents and actual incinerator and pyrolytic environments are vastly different from simple oxygen atmospheres. Refractories are used to act as a thermal barrier between the high temperature PAWDS environment and an ambient temperature outside the chamber skin to maximize safety to ships functions and personnel^D. Refractory suitability depends on its resistance to abrasion, maximum service temperature, corrosion resistance to liquids, gases and slag, erosion resistance, spalling resistance, resistance to thermal cycling, shock and fatigue from high thermal gradients, oxidation or reduction reactions, its mechanical strength, and its inspection and maintenance requirements. Refractories are available in either shaped (bricks) or unshaped, monolithic forms such as castable plastic refractories, ramming mixes, ceramic fiber blankets, or gunning mixes.

Table 3 - Melting Points of Common Refractories

Nomenclature	Formula	Melting Point (°C)
Corundum, Alpha Alumina	Al ₂ O ₃	2054
Baddeleyite, Zirconia	ZrO ₂	2700
Periclase, Magnesia	MgO	2852
Chromic oxide, Chromia	Cr ₂ O ₃	2330
Lime, Calcia	CaO	2927
Cristobalite, Silica	SiO ₂	1723
Carborundum, Silicon Carbide	SiC	2700 (sublimes)
Silicon Nitride	Si ₃ N ₄	1800 (dissociates)
Boron Nitride	BN	3000 (sublimes)

There are often property tradeoffs required to attain the desired optimum, serviceable refractory. Insulating refractories generally have lower density, strength, corrosion resistance, erosion resistance, and higher porosity and void fraction than stronger, less insulating refractories. Refractories are generally susceptible to thermal shock and spalling. Monolithic refractories are often more susceptible to thermal shock than shaped refractories. Dense

^D M. Heilberger, S. Chapelle, P. Valentine, "Development of a Thermal Destruction System for Treatment of U.S. Navy Shipboard Waste Using Plasma Arc Pyrolysis - Refractories and Slag Removal Methods - Survey and Evaluation", CARDIVNSWC-TR-63-95/05, General Atomic, Chapters 3,4, and 6 (June 1992).

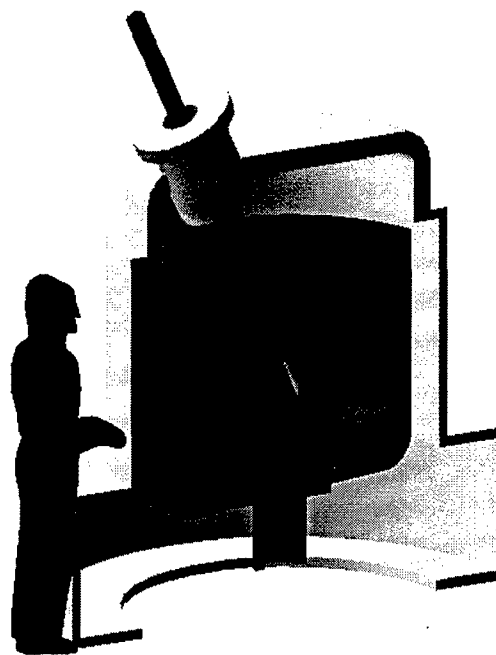


Figure 1 - Cross-section of refractory-lined hotwall PAWDS.

refractories tend to have high thermal conductivities, low porosity, relatively high strength, and improved corrosion resistance, but tend to be susceptible to thermal shock. Insulating refractories have higher porosity which improves thermal shock resistance, but provides numerous pathways for molten and gaseous materials to promote corrosion and spalling.

The corrosion resistance of refractories is based on the thermodynamics of the potential corrosion reactions, the reaction rates and kinetics of these possible reactions, the composition and form of the refractory material, and the surface chemistry of the refractory with corrosive gaseous, liquid, or solid environments. The spontaneous direction of the possible corrosion chemical reactions can be calculated which can indicate which reactions are theoretically possible. The reaction kinetics will be dependent on the specific environment (gaseous, liquid, or solid), surface chemistry, the material microstructure and composition, refractory phase(s), and the temperature. All ceramics or refractories used in an oxygen-rich environment are oxides or develop a protective oxide on their surface (such as SiO_2 on SiC or Si_3N_4). Though oxide ceramics are inert, and resist oxidation and reduction, they are not chemically inert. Ceramic corrosion between ceramic oxides and molten salt deposits generally can be explained as oxide/acid-base reactions.¹ To determine if a particular slag is acidic or basic, the ratio of lime to silica in the slag is commonly used. As a general rule the slag is basic if the CaO/SiO_2 ratio (or $\text{CaO} + \text{MgO}/\text{SiO}_2 + \text{Al}_2\text{O}_3$ ratio) is greater than one, If the ratio is less than one, the slag is considered acidic.² Gases and liquids can penetrate deeply into highly porous refractories which can exacerbate spalling and accelerated corrosion. Oxidizing gases such as NO_x , Cl_2 , O_2 , CO_2 , H_2O , and SO_2 , reducing gases (NH_3 , H_2 , C_xH_y , CO , and H_2S), and vapors of volatile elements and compounds may react with different refractories. Hydrodynamic mass transport

by either convection or diffusion can markedly affect the corrosion rate of a refractory in an environment. Non-wetting refractories are relatively resistant to corrosion with liquids or gases. Molten aluminum, iron, silica, and other constituents derived from the waste stream can react with the crucible refractory to form new compounds or phases which can have different melting temperatures, dimensional stabilities, and corrosion resistances. The new phases or compounds can cause dimensional changes which can cause problems in the chamber. High purity refractories are more corrosion-resistant because certain minor impurity components have microstructures, phases, and defect structures which can introduce significant corrosion. High purity refractories improve corrosion resistance by avoiding low-melting eutectics. Alkali impurities should be minimized as much as possible. Solids, either as fine particulates or dust, can cause degradation of refractories through abrasion or deposition.

Silicon carbide, high alumina, and alumina-chromia refractories were considered the best candidates for a working refractory in a hotwall PAWDS. Alumina-based refractories are usually available with silica and generally offer good corrosion resistance. However, high alumina refractories degrade rapidly in HF, chlorides, molten or strong hot aqueous alkalis, and some molten metals.³ Alkalis flux the alumina-silica system. Chlorides cause increased porosity and removal of alumina or silica. Chromia (Cr_2O_3) improves the corrosion resistance of high alumina refractories, by reducing slag or liquid penetration.⁴ Favorable performance of alumina-chromia occurs even when the slag has a high iron content, but the use of chromia may introduce environmental questions. Silica contained in high alumina refractories reacts with iron oxide and alkalis from slag to form a glassy surface layer over the refractory which eventually exposes new surfaces to further reaction. Silicon carbide is not attacked by acids, but reacts readily with fused caustic, halogens, and certain metal oxides. Silicon carbide is also abrasion resistant and less prone to thermal shock than other refractories.⁵ The operating temperature of SiC should be limited to 1300 °C in reducing $\text{N}_2\text{-H}_2\text{-CO}$ environments when no steam is present.⁶ Other refractories such as Si_3N_4 and ZrO_2 are considered too expensive to use in a full-size PAWDS. Some of these working refractories are listed in Table 4.

There are several limitations to the use of refractories in the PAWDS design. First, a layer of a working refractory such as high purity alumina, silicon carbide, or alumina-chromia is required to be used since these refractories have the highest resistance to corrosion reactions with slag, liquids, or gases, are abrasion and spall resistant, have low porosity, and have a limited thermal shock resistance. Since these refractories also have a high thermal conductivity, an insulating refractory must be inserted between the chamber shell and the working refractory. To reduce the temperature from 1500 °C on the inner wall surface to about 100 °C on the outer shell, the combined thickness of the two refractory layers can be 12 inches (30 cm) or more. This adds an unacceptable weight for a shipboard PAWDS capable of processing the level of solid wastes generated by the fleet.

Second, refractories may crack because of thermal shock and react with the shipboard waste to corrode or wear away, thus requiring repair. Eight or more hours are required for the crucible chamber to cool before repairs can initiate. Repair would require the use of plastic refractories, mortar materials, or patching mixes for quick repairs or more a more time-

Table 4 - Candidate Working Refractories^{2,49}

PARAMETER	CarboFrax® M SiC	Alfrax®	Refrax ®20 SiC	Tuflin® 95DM	Aurex® 75 SR	Corundum® DM	Ruby® SR
Composition	89.2-SiC;0.5-CaO;1.0 Fe ₂ O ₃ 1.0-Al ₂ O ₃ ; 6.3-SiO ₂	96-Al ₂ O ₃ ; 3.9-CaO tr-others	75-SiC 23.4-Si ₃ N ₄ tr-others	94.2-Al ₂ O ₃ ; 2.0 SiO ₂ ; 3.6- other oxides, 0.1- Fe ₂ O ₃ ,CaO	72.6- Cr ₂ O ₃ 20.7-Al ₂ O ₃ ; 5.7- ZrO ₂ 1- other oxides	99.7 -Al ₂ O ₃ ; 0.2-SiO ₂ 0.1- Fe ₂ O ₃	83.6-Al ₂ O ₃ 10.2-Cr ₂ O ₃ 1.9-SiO ₂ ; 3.5- other oxides
Max. Operating Temperature, °C	1480	1815	1760	1870	>1925	1870	1815-1870
Density g/cm ³ /lb.ft ³	2.33/145	2.73/170	2.62/163	3.35/209	4.08/255	3.33/208	3.19/199
Apparent Porosity, %	17	--	15	12	15.8	12.9	18.1
Thermal Cond. @1477°K W/m°K	15.7	--	16.3	3.60	2.59	2.45	3.31
Permanent linear change, % 20-1727°C	-0.1 (est)	--	--	-0.1	+0.3	negligible	-0.2
Thermal shock resistance (2)	--	--	--	40+ cycles	14 cycles	3 cycles	22-25 cycles
Rupture modulus (MPa/psi)	20.7/3000	38.6/5600	43.4 /6300	20.8/3020	14.2/2060	31.0/4500	14.3/2080
Compressive Strength (MPa/psi)	138/20,000	--	138/20,000	---	58.6/8500	---	87.6/12,700

Carbofrax, Alfrax, Refrax are registered trademarks of The Carborundum Company

Tuflin, Aurex, Corundum, and Ruby are registered trademarks of Harbison-Walker, a division of INDRESCO, Inc

consuming reinstallation of refractory brick. Refractory repair work would require specialized training of shipboard personnel and an assignment of larger number of shipboard personnel to a PAWDS operation. This is counter to the present downsizing "Smartship" philosophy of the U.S. Navy. Storage of patch materials or replacement crucible/chambers is also not feasible because of size and weight limitations.

Cold Wall Design

Driving forces for a cold wall design include the reduction of weight and size, improvement of reliability, operability and maintainability, and increased safety, while maintaining environmental compliance of the PAWDS. The gas temperature in the primary chamber is about 1200 °C with possible hot spots above 1370 °C. Thermal shock occurs during start-up, shutdown, and in the event of water leaks. The chamber environment would contain N₂, CO₂, H₂O vapor, NO_x, and small quantities of alkalis and acid gases (HCl, SO₂). Particulates in the gas stream could cause erosion and abrasion damage. A conventional refractory wall consisting of a working refractory and insulating refractory would be over 12 inches (30 cm) thick and weigh 120 lb/ft². A more advanced commercial refractory wall of ceramic fiber and a working refractory is about 7 inches (18 cm) and weighs 70 lb/ft². Both conventional and advanced refractory walls would have a limited life expectancy.

A light-weight refractory wall was proposed for a PAWDS with about a 4-inch (wall) and predicted to have a 10,000 hour life^E. As shown in Figure 2 the light-weight wall consists of a thermal barrier coating (TBC) on a 1-1.3 cm thick superalloy shell such as UNS N07718. The TBC/superalloy wall is cooled by air. A ceramic fiber insulation layer is placed between the air-cooled channel and an outer water-cooled jacket. The TBC consists of a partially stabilized zirconia (PSZ) about 150 μm thick and an MCrAlY (M=Ni or Co) bond coating about 50-75 μm thick for corrosion protection and resistance to high temperature oxidation. This technology has been successfully employed for use in marine gas turbines to prolong the life of alloys in high temperature areas for times exceeding 10,000 to 12,000 hours^F. The TBC serves to reduce the substrate alloy temperature by up to 300 °F (150 °C).⁷ The thermal barrier coating can be applied by either air plasma-spraying (APS) or electron beam-physical vapor deposition (EB-PVD). The bond coat reduces the stresses and the temperature gradient between the PSZ layer and the alloy substrate. APS provides slightly better heat insulation while EB-PVD coatings have superior spalling resistance. Failure of APS coatings appear to occur under oxidative thermal cycle conditions by the formation and linkage of microcracks with the zirconia layer just above the bond coat.⁸ EB-PVD coatings are believed to fail primarily from cracks that develop within the thermally grown oxide that forms on the bond coat surface.⁹ It is for this reason that the preferred cooling is via air and not by water since the latter causes increased thermal stresses and induces premature failures of the TBC. The PSZ usually consists of about 8% yttria stabilized zirconia, but this type of PSZ is susceptible to degradation by steam at 100-200°C¹⁰, by molten salt deposits from sulfide, vanadium, and sodium fuel contaminants, and by P₂O₅ and various sodium phosphates at 700 and 900 °C.^{11,12} Zirconia-based TBC can be stabilized with scandia (Sc₂O₃) rather than yttria to avoid many hot corrosion problems.¹³

A water-cooled design for the PAWDS, shown in Figure 3, consists of an eductor with a plasma torch pyrolyzing the waste material as it is drawn through the tube, around the plasma torch, and into a secondary combustion chamber. The eductor has a coil of cooling tubes brazed to the outside of a metal tube. Inside of this tube a layer of felted insulating fiber slows the heat loss from the inner iron or nickel-based alloy liner. The inner liner is maintained between 900 and 1000 °C. The ability of the liner alloy to resist corrosion is dependent on its protective surface oxide film. Conditions which can damage the oxide and the substrate alloy in PAWDS are probably similar to that experienced in waste incinerators such as: (1) alternating oxidizing and reducing environments at high temperatures which may interfere with oxide formation and oxide maintenance resulting in porous films; (2) mechanical stresses such as residual stresses derived from fabrication and welding processes, cyclic thermal stresses that deform the alloy substrate because of rapid cooling rates, or crack or spall the oxide layer

because of tensile or compressive stresses; (3) impingement/erosion which removes the oxide when fluid (gas or liquid) flow exceeds a threshold velocity; (4) reaction with corrosives, moisture condensation; (5) deposits of low-melting point mixtures; (6) flame impingement; (7)

^E Plasma Arc Waste Destruction System (PAWDS) - Mid-Term Status Review, MSE Technology Applications, Inc., PERMA, Inc., Applied Ordnance Technology, Inc, April 18, 1996

^F Private Communication, Robert Clarke, Code 613, CDNSWC

crevices or defects encouraging galvanic attack; (8) changing metal properties with prolonged exposure at high temperatures; (9) chlorides; and (10) alkali sulfates.¹⁴ Reaction of the slag with the chamber wall must also be considered.

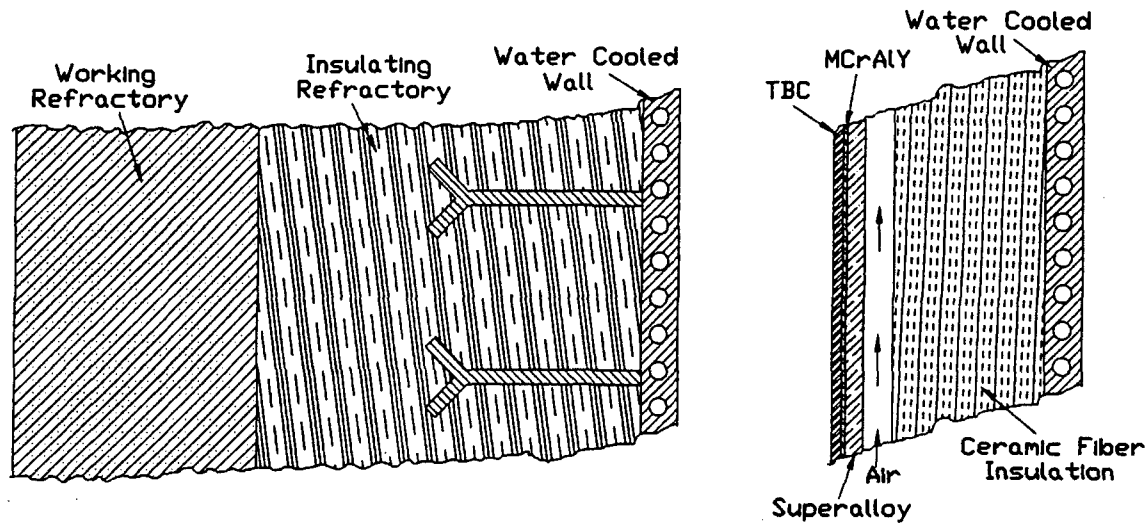


Figure 2 - Comparison of thick, conventional refractory wall required for hotwall PAWDS design (left) with a light-weight, air-cooled coldwall design using a TBC on a superalloy (right).

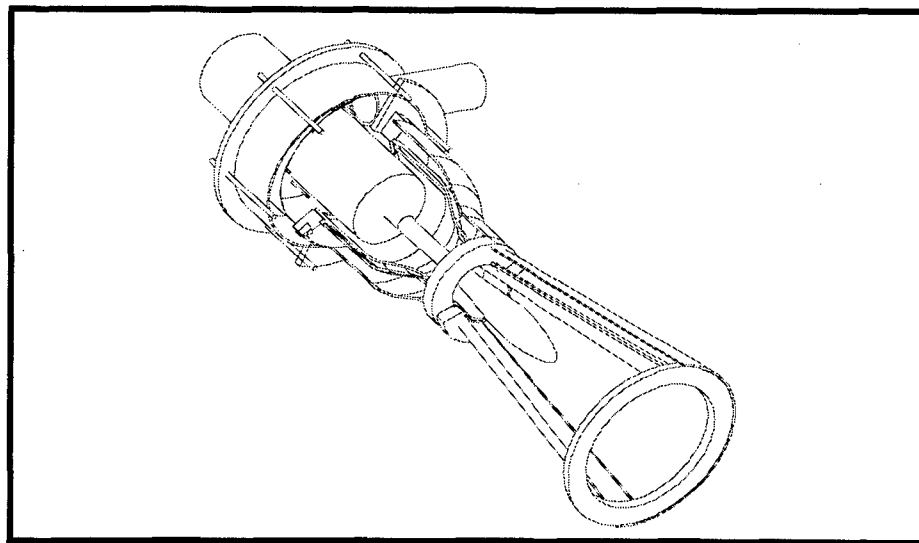


Figure 3 - Diagram of eductor consists of a central plasma torch which will process organic shipboard waste drawn through the tube and into a secondary chamber.

A number of candidate alloys (Tables 5 and 6) have been considered for the coldwall primary reaction chamber and components of the PAWDS. Wall temperature is a major factor in determining the best material. The specific environment in the chamber (temperature,

corrosive constituents in feed, air-cooled versus water-cooled, etc.) also will contribute to many possible corrosion problems. The internal surface temperature of a water-cooled primary chamber is around 330-530 °C while an air-cooled chamber will have a surface temperature of about 1000 °C. The actual chamber temperature will dictate the available materials for providing reliable, long-term service for a PAWDS.

Table 5 - Candidate PAWDS Alloys - Chemical Compositions ⁴⁶⁻⁴⁸

Alloy ASME or UNS Number	C	Mn	P	S	Cr	Ni	Co	Mo	Si	Cu	Fe	Al	Ti	W	Cb+Ta	Others
SA 414 Gr A	0.15	0.90	0.035	0.040							bal					
K11789	0.17	0.40- 0.65	0.30	0.30	1.00- 1.50	---	---	0.45- 0.65	0.50- 0.80	---	bal	---	---	---	---	---
S31008	0.08	2.00	0.045	0.030	24.00- 26.00	19.00- 22.00	---	---	---	---	---	---	---	---	---	---
S31603	0.03	2.00	0.045	0.03	16.0- 18.0	10.0- 14.0		2.0-3.0	1.00							
N06022	0.010	0.50		0.08	22	56	2.5	13	0.08	--	3			3		0.35
N06059					23 nom	59 nom		16 no			1 nom					
N06455	0.01	1.0	0.025	0.010	14.0- 18.0	bal	2.0	14.0- 17.0	0.08		3.0		0.70			
N08366	0.03	2.00	0.030	0.003	20.0- 22.0	23.5- 25.5		6.0-7.0	0.75							
N06600	0.10	1.00		0.015	14.00- 17.00	72.00 min	---	---	0.50	0.50	6.00- 10.00	---	---	---	---	---
N06601	0.10	1.0		0.015	21.0- 25.0	58.0- 63.0			0.50	1.0	rem	1.0-1.7				
N06625	0.10	0.50	0.015	0.015	20.0- 23.0	55.0 mi	1.00	8.0- 10.0	0.50- -	---	5.00	0.40	0.40	----	3.15- 4.15	---
N06671	0.05 nom				48.0 no	bal							0.35 nom			
N06690	0.03 nom				30 nom	60.5 nom					9.5 nom					
R30556	0.05- 0.15	0.5- 2.0	0.04	0.015	21-23	19-22.5	16-21	2.5-4.0	0.2- 0.5	---	bal	0.10- 0.50	---	2.0- 3.5	0.30- 1.25 T ;0.30 Nb	0.005- 0.10 La; 0.001- 0.10 Zr; 0.10-0.30 N; 0.04 B
N12160	0.05	0.5			28	37	30	1	2.75	---	3.5 ma	---	0.45	1	1.0 max	
N08120	0.05	0.7			25	37	3	2.5	0.6	---	33	0.1	0.1	2.5	0.7	0.004 B;0.2 N
N07214	0.5 no	0.5			16 nom	75 nom	---	---	0.2	---	3 nom	4.5 nom	---	---	---	0.1 Zr;0.01 B; 0.01 Y nom
N06230	0.05- 0.15	0.3- 1.0			20.0- 24.0	bal	5	1.0-3.0	0.250 .75		3	0.20- 0.50		13.01 5.0		0.005-0.50 La;0.015 B
N07041	0.05- 0.12	0.10		0.015	18.0- 20.0	55.0 nom	10.0- 12.0	9.0- 10.50	0.50		<0.3	1.40- 1.60	3.0- 3.30			0.0030-0.010 B
R30188	0.05- 0.15	1.25			20.00- 24.00	20.0- 24.0	bal	---	0.200 .50	---	3.00	----	---	13.01 6.0	---	0.03 -0.15 L

Table 6 - Candidate Alloy Physical and Mechanical Properties ⁴⁶⁻⁴⁸

Alloy UNS Number	ASME max temp other max service temp °C	ASME strengt h criteri	1% Creep- rupture strength 500 C/10 ⁵ h.	Thermal conductivi ty W/m- °K 500 °C	Thermal conduct. W/m- °K 800 °C	Expan. Coeff. µm/m- °C 500 °C	MP °C	Density g/cm ³	Specific Heat kJ/kg-°K @ 871°C	UTS ks @ 982°C	0.2% YS ksi @ 982°C	Percent elong. @ 982 °C
SA414-A	400-500	425	4.5-6 ksi	40	26	16.4						
SA213- T22	580 °C	595	6.5-7.3 ks	37	26	15.4				2.4 max @650° C		
S31008			13			17.5		8.00	0.500 @100	13	---	57
S31603	760	815	19 est.							6.1 max @650° C		
N06600	982			22.5	27.6	15.1	1393	8.498	0.625	7.5	4.0	118
N06601				19.5	24.4	15.2	1301- 1368	8.11				
N06625			649 -27.5 871-2.5ks 10 ⁵ hr	16.9	21.4	13.9	1288- 1349	8.442	0.620	25.8	13.0	143
N06671						15.0	1305- 1350	7.86	0.456 RT.	14	9	
N06690				22.1	26.6	16.2 @ 649 °C	1345- 1375	8.08	0.6 est	15	10	
R30556	900	650		18.3	22.7	16.2		8.23	0.600	30.3	20.2	56
N12160	816		16.3 @ 593	19.8	26.1	14.9			0.562	20.4	10.8	90
N08120				18.7	24.9	16.1			0.558	27.9	19.4	81
N07214			16 @ 760	21.0	29.7	14.8	>1345	8.05	0.724	16	7	80
N06230	899	899	11.5 @ 760			14.0	1301- 1371	8.97	0.605	32.5	17.3	70.5
N07041							1252- 1371	8.25	0.452	90@87	50@892	19
R30188			13.5 @ 760	19.3	24.8	14.6	1302- 1330	9.13	0.568	37.7	24.7	86

Corrosion in High Temperature Environments

Candidate materials for high temperature waste pyrolysis need to be corrosion resistant under a number of potential degradation processes which can occur in waste incineration systems or thermal pyrolysis: (1) oxidation, (2) carburization, (3) sulfidation, (4) chloridation, (5) hydrogen interactions, (6) hot corrosion, (7) dewpoint, acid corrosion, (8) galvanic corrosion, (9) crevice corrosion, (10) localized, pitting corrosion, (11) impingement, erosion-corrosion, (12) liquid metal embrittlement, (13) aging reactions, sensitization, (14) creep damage, (15) fatigue and corrosion fatigue, and (16) environmental cracking.

As mentioned previously, most metals and alloys in an oxidizing environment are protected to varying degrees by an oxide layer. Iron oxides alone are not protective above 550 °C.¹⁵ Oxidation of carbon steels from air or steam forms an oxide scale along the metal surface which grows and thickens with time. The scales, depending on chemical composition, can be mildly insulative to very insulative. The scale growth rate increases with a rise in temperature. Chromium, aluminum, and/or silicon assist in forming scales which are more protective at

higher temperatures.¹⁶ Chromium oxide is stable up to 983 °C above which the oxide volatilizes to gaseous CrO₃. Mechanical damage by spallation or cracking of the oxide film from cyclic oxidation of chromia and alumina oxides formed on nickel-based alloys is due to the mismatch of thermal expansion coefficients between the oxide and the base alloy.¹⁷ Small additions of lanthanum, yttrium, tantalum, ceria, zirconia, and/or niobia improve the scale adhesion and scale resilience to cyclic oxidation.¹⁵ Table 7 lists the degree of corrosion damage from commercial tests in static and dynamic, cycling environments as well as other probable corrosive scenarios which can be expected in the shipboard PAWDS.

Table 7 - Corrosion in Various High Temperature Environments⁴⁸

ALLOY UNS number	Static Air Oxidation Temperature ¹		Dynamic Air Oxidation Temperatur e ²	Reducing Sulfidation ^{3,4}		Hot Corrosion ^{5,8}		Chloridation ⁶	Carburiza tion ⁷ mg/cm ² / mil depth
	980 °C	1204 °C		871 °C	593 °C	675 °C	760 °C		
S31008	1.1	10.3	16.5	14		12	13.0 (35)		7.7/84.2
N06601	1.3	2.6 @1090 7.5**	20.0	perforated >21.7				9.0 @ 900	
N06625	0.7	>47.6	7.6			5		10.5 @ 900	
N06690							2.8(nil)		
N07214	0.2	0.7	1.2					6.0@900	
N08120	3.7	7.7 @1090							0/0
R30556	1.1	>150	6.2	35.6	121	2.5		6.0@ 900/11.8	1.0/18.0
N06230	0.7	7.9	3.5						0.4
R30188	0.6	>21.7	4.2	23.6	151		46.6 (9)		0.5

1) Average metal affected, results in mils (0.001" = 1 mil) Static Oxidation in Air ; lab test for 1008 hour with specimens cycled to room temperature once every 168 hours, ** large internal voids not included for N06601 reading.

2) Maximum metal affected, results in mils (0.001" = 1 mil) Dynamic Oxidation in Air ; lab test for 1000 hour with specimens cycled to room temperature once every 30 minutes

3) Ar- 5%H₂- 5% CO-1% CO₂- 0.15% H₂S, PO₂ = 3x10⁻¹⁹ atm, duration 500 hours except 310SS which was for 215 hours, maximum depth of attack

4) H₂-46% CO-0.8% CO₂- 1.7% H₂S at designated temperatures.

5) Recuperator of aluminum remelting furnace flue gases. Mode of corrosion combined attack by alkali sulfates, chlorides with oxidation for 1150 hours, maximum metal affected.

6) Ar+20% O₂-- 0.25% Cl₂ for 400 hours at 1000 °C, average metal affected, mils.

7) packed Carburization resistance for 500 hours in packed graphite , mg/cm² at 982 °C.

8) Burner rig test with combustion products of No. 2 fuel oil (1.0 % sulfur), thermal shock frequency 11/500 hours, average corrosion rate, corrodent urine; mils/year (max penetration, mils).

Carburization alone usually does not result in corrosion or alloy wastage, but adsorption and diffusion of carbon into the base alloy can lead to significant changes in the alloy mechanical properties and leading to possible alloy embrittlement. Carbon dioxide produced in an oxidizing environment is less corrosive than carbon monoxide, CO, which is the prevalent carbonaceous gaseous species in a reducing environment. Stainless steels will react with hydrocarbons and/or carbonaceous gases at elevated temperatures to carburize at its surface. Under conditions where hydrocarbons are present in the gas stream and/or with the introduction

of oily components, nickel-based alloys are susceptible to severe carburization called "green rot".¹⁸ Green rot occurs when internal chromium carbides are formed during carburization; subsequent oxidizing of the carbides at the grain boundaries may result in embrittlement. Deterioration and material wastage by metal dusting in carburizing gases at 426-815 °C result in pitting and overall wastage of stainless steels with or without an oxidizing environment.^{19,20} Corrosion products in the pits consist of metal carbides, metal oxides, and graphite. The attack is localized and carburization is confined to the pit. Metal dusting has been encountered in chromia-containing alloys such as ferritic and austenitic stainless steels, nickel-chromium alloys, and cobalt-chromium alloys. Nickel-based alloys are more resistant to carbon diffusion than most other alloys and alloys with higher nickel content are superior to low-content nickel alloys. Carburization appears to be appreciable in nickel alloys at 650-700 °C (penetration 0.2-0.8 mm in 50-55 days). Nickel-chromium alloys containing titanium, niobium, and aluminum are better than basic nickel-chromium alloys in CO₂ atmospheres at 700-800 °C. The Al₂O₃ scale appears to be much more resistant to carburization than the Cr₂O₃ scale.²¹

Sulfidation is a reaction of a metal or alloy with a sulfur-containing species to produce a sulfur compound that forms on or beneath the surface of the material. In most environments, Al₂O₃ or Cr₂O₃ form preferentially to the sulfides, but destructive sulfidation attack occurs at oxide crack sites.²² The reduced species, H₂S, is more corrosive than the oxidized species, SO₂. Sulfates are contained in marine air used in cooling shipboard systems. Sulfidation of nickel results in the formation of eutectic Ni₃S₂ which has a melting point of 635 °C with sulfur solubility of 0.005 %.²³ This eutectic formation causes the initiation and propagation of intergranular corrosion. Chromium improves resistance to sulfide attack. Increased chromium content increases the temperature limit in a sulfidizing environment. Chromium sulfide formed below the surface of the protective oxide layer may lead to depletion of chromium and breakaway corrosion. Nickel-chromium alloys have been successfully used at service temperatures of 750-1200 °C. Manganese, silicon, and aluminum additions improve the resistance of nickel alloys to sulfur attack.²⁴

Chlorides accumulate rapidly on metallic surfaces of a test probe. Typical deposits contained 21-27% Cl when the flue gas contained 40-140 ppm HCl.²⁵ Municipal wastes were characterized by Krause as having a 0.5% halide dry content of which 60% was derived from organic, polymer sources.²⁶ Chloride salts have melting temperatures as low as 175 °C, which can act as a fluxing agent and dissolve protective oxide films. Air in a marine environment used in cooling the hotwall surfaces of a shipboard PAWDS will be laden with chlorides. Molten SnCl₂ (m.p. 246 °C), SnCl₂ + NaCl (m.p. 199 °C), ZnCl₂ (m.p. 283 °C), eutectic PbCl₂/FeCl₃ (m.p. 175 °C), and eutectic ZnCl₂/NaCl (m.p. 262 °C)²⁷ may cause rapid corrosion of carbon steel, if present. Attack by halogens at elevated temperatures occurs through the volatility of the reaction products. Oxides that form in combustion gases will be porous and prone to fracture. Stainless steels are generally passive, but surface pitting may occur in chloride-containing environments. Nickel-based alloys can be expected to have superior corrosion resistance as compared to stainless steel alloys.²⁸ Clay containing aluminum silicate may inhibit chloride-related corrosion by raising the melting points of chloride salts through the formation of sodium aluminum silicates which expel HCl and SO₃.²⁹ Problems

with chlorides can be mitigated if plastic is removed from the waste stream and remaining sources of chlorides in the solid waste stream are minimized. Increasing the oxygen content and adding water vapor has also reduced the corrosion rate of various alloys by chlorides in a simulated waste incinerator environment.³⁰

Steam may decompose on metal surfaces at elevated temperatures to form hydrogen and oxygen. The plasma torch in the PAWDS is capable of producing atomic hydrogen and atomic oxygen. Loss in tensile ductility of steels and nickel-based alloys has been observed in gaseous environments with a total hydrogen content of 0.1 to 10 ppm at -100 to 700 °C. Hydrogen attack or hydrogen damage occurs when gaseous hydrogen diffuses into the steel and reacts with the carbides to form methane, $4\text{H} + \text{Fe}_3\text{C} \Rightarrow \text{CH}_4 + 3\text{Fe}$, and internal microcracks leading to brittle rupture. The reaction rate is dependent on hydrogen concentration, diffusion, and total gaseous pressure and occurs at 200-600 °C. Hydrogen damage has been observed in utility boilers as low as 316 °C.³¹ Atomic hydrogen diffuses readily in steel which may cause cracking and decarburization of steel. Hydrogen damage can occur in other high-strength alloys resulting in loss of tensile ductility. Nickel alloys are much less susceptible to hydrogen damage than ferrous-based alloys.

Hot corrosion is the degradation of materials by the presence of a liquid deposit or ash. Type I corrosion occurs primarily at metal temperatures ranging from 850 to 950 °C. This attack involves molten ash and deposits containing sodium sulfate and/or potassium sulfate salts. Very small amounts of sulfur and sodium or potassium can produce sufficient Na_2SO_4 . In gas turbine environments, a sodium threshold level below 0.008 ppm by weight precluded type I hot corrosion. Other impurities such as vanadium, phosphorus, lead, chlorides, and unburned carbon can be involved in lowering salt melting temperatures. High chromium content (> 25-30% Cr) is required for good resistance to hot corrosion. Nickel alloys with chromium and aluminum show improved resistance to hot corrosion.

Type II or low temperature hot corrosion occurs in the temperature range of 650 to 750 °C. This type of hot corrosion involves a gaseous reaction of SO_3 or SO_2 with CoO and NiO which results in pitting from the formation of low melting mixtures of Na_2SO_4 in Ni-Cr, Co-Cr, Co-Cr-Al, and Ni-Cr-Al alloys (32). If other reactants are added, melting temperatures can be further lowered. In the presence of molten ash products, the oxide, even in oxidizing environments, becomes unstable and dissolves. Alkali sulfates deposited on the fireside surfaces of boilers may react with SO_3 or SO_2 to form alkali pyrosulfates (m.p. 400-480 °C) or alkali-iron trisulfates.³³ A NaCl- $\text{Na}_2\text{S}_2\text{O}_7$ mixture can have a eutectic melting temperature of 622 °C. Molten pyrosulfates (such as $\text{Na}_2\text{S}_2\text{O}_7$) reacts with carbon steels at 335-410 °C by dissolving the protective oxide film and then reacting with iron to cause accelerated wastage. A few ppm of vanadium accelerates this reaction. The melting point of these deposits on waterwall tubes ranges from 335 to 410 °C. Several references have evaluated the corrosion resistance of different alloys in incinerator environments.^{14,34,35}

When the PAWDS is shutdown during idle periods or while the ship is at port, temperatures can fall below the condensation temperature of flue gases containing HCl and/or

H₂SO₄, and may form aqueous solutions of these acids. The dewpoint temperature of sulfuric acid (SO₃+H₂O) is 120-150 °C and rises with an increase in SO₃ concentration, but above 35 ppm the dewpoint temperature is constant at 150 °C. HCl has little effect on carbon steel below 260 °C, but in an excess of air, may form FeCl₂ on the carbon steel surfaces. Austenitic stainless steels subjected to moist deposits high in chlorides can suffer from chloride stress corrosion cracking.³⁶

Galvanic corrosion can occur if two metals of different electrochemical potentials are adjacent and electrically connected. Galvanic action also can proceed for the same metal if present at significantly different temperatures. At temperatures where gases prevail (400-1700 °C), the electrical conductivity should be low enough that galvanic action would not likely be a problem. The relatively noble potential of nickel-based alloys and stainless steels will not generally cause galvanic effects.

Carbon is more cathodic than platinum in the galvanic series for seawater and may be equally cathodic to the candidate chamber alloy in the PAWDS environment. The corrosion rate due to galvanic effects will be dependent on the conductivity of the steam/gaseous environment and the temperature fluctuations along the crucible wall. Deposition of soot (carbon) on the chamber walls may lead to galvanic attack if the conductivity of condensed fluids during idle periods is sufficiently high. Large sooted areas versus bare steel areas could increase the severity of galvanic attack. Soot or deposits may be porous and can lead to concentration of deleterious constituents through the porous layer. For instance caustic levels, caused by selective deposition of NaOH at high heat flux areas, have concentrated 100 ppm NaOH in bulk boiler water to over 200,000 ppm through a process called wick boiling.³¹

Compositional changes of liquids or gases in crevices may be severe. Crevices may be formed at mechanical joints or under porous, but occluding deposits. Crevices leading to severe corrosion can occur if oxidizing conditions and a soluble species are present; such conditions usually occur during idle times when moisture is present.¹⁴ Alloys high in molybdenum typically possess higher resistances to pitting and crevice corrosion attack. Surface deposits or crevices formed by joints or connections may be subject to crevice corrosion of stainless steels. Gasket materials containing sulfur or graphite can also accentuate crevice corrosion.

Grain boundary segregation may result in localized corrosion if the grain boundaries are not as resistant as the alloy matrix or segregation causes depletion of corrosion resistant elements. Pitting is another form of localized corrosion. Both dissolved oxygen and carbon dioxide can promote pitting of carbon steels. An alkaline pH can diminish corrosion with the evolved gases likely to be neutral to acidic. Ash deposition, thermally induced stress, and particulate erosion may cause conditions that accelerate localized corrosion by cracking the protective oxide layer. Grain boundaries may be susceptible to operating conditions or room temperature corrosion when condensed water solubilizes corrodents from deposits or soot.

In the shipboard PAWDS, the components may be subjected to ash and soot deposition, thermally induced stresses, and possible particulate erosion.¹⁴ The primary chamber wall may suffer from erosion if the flame, high-velocity gases, or particles impinge on the wall. Local reducing conditions will increase the rate of erosion over conditions existing in oxidizing environments due to the increased difficulty of the alloy to repair and reform a passive oxide film. Flame impingement can produce local overheating which can cause distortion. Erosion may also cause protective scale removal. Impingement of liquid spray droplets on hot walls could cause spalling, dissolution, or erosion of the oxide layer. Alloy modification for erosion resistance may not be compatible with corrosion resistance. Stainless steels and most nickel-based alloys generally provide good resistance to impingement or erosion.

The crucible alloy material reportedly will be protected from molten slag by a oxide/slag skull in the PAWDS. However in the event of possible contact with molten slag, it is important to know the corrosion resistance to slag of the candidate materials. Liquid metal corrosion may cause dissolution of a surface directly, by intergranular attack, or by leaching. Liquid metal attack may also initiate alloying, compound reduction, or interstitial or impurity reactions. Carbon and low alloy steels are susceptible to various molten metals or alloys such as brass, aluminum, bronze, copper, zinc, lead-tin solders, indium, and lithium at temperatures from 260 to 815 °C. Plain carbon steels are not satisfactory for long-term usage with molten aluminum. Stainless steels are generally attacked by molten aluminum, zinc, antimony, bismuth, cadmium, and tin.³⁷ Nickel, nickel-chromium, and nickel-copper alloys generally have poor resistance to molten metals such as lead, mercury, and cadmium. In general nickel-chromium alloys also are not suitable for use in molten aluminum.³⁸ Liquid metal embrittlement (LME) is a special case of brittle fracture that occurs in the absence of an inert environment and at low temperatures.³⁹ Decreased stresses can reduce the possibility of failure in certain embrittling molten alloys. Stainless steels suffer from LME by molten zinc. Small amounts of lead will embrittle nickel alloys, but molybdenum additions appear to improve lead LME resistance. There are no known metals or alloys totally immune to attack by liquid aluminum.⁴⁰ The selection of fabricating processes must be chosen carefully for nickel-based superalloys. Liquid metal embrittlement can occur when brazing precipitation-strengthened alloys such as UNS N07041.⁴¹ Many nickel superalloys crack when subjected to tensile stresses in the presence of molten (B-Ag) brazing filler alloys.

Long-term aging effects can cause metallurgical changes that alter the mechanical and corrosion properties of materials. Graphitization is a microstructural change that can occur in carbon and low alloy steels. Pearlite (alternating ferrite and Fe₃C platelet structure) normally found in such steels will transform in time to graphite and ferrite at temperatures above 425 °C which causes loss of ductility and promote embrittlement. Alloying additions of at least 0.7% Cr and 0.5% Mo to steels markedly improve resistance to graphitization. Weld sites are particularly susceptible to graphitization. Heat treatments or operating conditions that heat ferritic and austenitic stainless steels to 500-900 °C cause segregation at the grain boundaries by the precipitation of complex chromium carbides, the formation of sigma phase or the precipitation of other deleterious phases. The properties of precipitation-strengthened superalloys (processed at 535-815 °C) such as UNS N07041 may be altered by brazing.⁴¹

Normal welding can induce susceptibility of stainless steels without postweld heat treatment. Careful control of heat treatment can avoid intergranular corrosion of unstabilized stainless steels containing more than 0.03% C. Nickel-based superalloys are also susceptible to grain boundary segregation. Nickel-based superalloys can be embrittled by less than 20 ppm sulfur segregation to alloy grain boundaries.

PAWDS candidate materials such iron, nickel and cobalt superalloys owe their unique strength up to a fairly high threshold temperature to the presence of strengthening particles such as inert oxide dispersoids, carbides, coherent ordered precipitates, and solid solution strengthening agents in a face-centered cubic (with appropriate nickel additions) structure. Introduction of precipitates into the alloy through solid solution reactions require specific alloy chemistries and heat treatments to achieve the desired mechanical properties.^{41,42} However, at prolonged exposures to high temperatures (760-1000 °C), the phase rule alone suggests that a large number of new phases could nucleate within multicomponent superalloys to form a number of microstructural instabilities.⁴³ These instabilities can include transformation of a metastable phase to a more stable, but incoherent phase as in carbide transformation, stress induced differential diffusion of solute atoms (coarsening of $M_{23}C_6$ at grain boundaries), or dissolution of strengthening precipitates in critical areas of the microstructure. Structural instabilities of superalloys at elevated temperatures can also include the formation of new phases such as sigma, mu, and Laves phases which are brittle and possess crack-like morphologies that can adversely affect alloy tensile and stress rupture ductility and impair resistance of the alloy to crack growth.⁴³

Creep is a time-dependent strain of a material under stress. Rupture of a metal or alloy can occur when it is subjected to stress at elevated temperatures for a sufficiently long time. Stresses are significantly lower than that necessary to cause rupture in room temperature or during short-term tensile tests. Higher temperatures and/or higher stresses will tend to decrease the time required for creep rupture. Creep embrittlement can occur in the temperature range of 425-595 °C for alloys having a ferrite and carbide microstructure.⁴⁴ The embrittlement is most detrimental after the steel has been cooled below 260 °C. For temperatures above 760 °C, metallic liners will have a limited life because of the microstructural instabilities that develop in many of the superalloys with prolonged exposure. One possible alloy is UNS N06671⁴⁵ which can be used to 980 °C with temperature excursions of 1100 °C.¹⁴ This alloy, however, is not widely available and is difficult to fabricate. Other possible selections would be alloys UNS N07041 and UNS N06230, which have good high-temperature strength and resistance to long-term thermal degradation. However, their resistance to hot corrosion, sulfidation and chloride-containing salts is not known.

Frequent cycling may reduce the design life of the PAWDS walls from that predicted for operation at steady state. The hot gas environment within the PAWDS will influence the corrosion fatigue resistance of candidate alloys.⁴⁶ Cyclic temperature conditions accelerate attack mainly through the loss of the protective scale.¹⁴ Depending on the severity of the thermal cycles in the water-cooled design, spallation of thermal barrier coatings, chromized, and aluminized coatings is probable. Corrosion fatigue is the combined action of a repeated or

fluctuating stress and a specific corrosive environment that usually lowers the minimum stress level and/or the number of cycles that will cause failure than in an inert environment. Corrosion fatigue cracking and stress corrosion cracking often initiate at stress risers such as pits. In certain instances such as in nickel-based superalloys in high-temperature oxidizing environments, the aggressive conditions can slow the fatigue fracture propagation. Stainless steels have good corrosion-fatigue limits when compared to other steels.

Stress corrosion cracking (SCC) is a brittle fracture of an otherwise ductile material which occurs under the combined action of a residual or applied tensile stress and an alloy-specific corrodent. SCC is affected by alloy composition and heat treatment, the exposure time, temperature, and solution medium. Fluctuating temperatures can accelerate stress corrosion cracking of austenitic stainless steels in the presence of chlorides, particularly at high stress points from design, operation or fabrication. Nickel alloys have improved resistance to environmental cracking over steels and stainless steels although nickel alloys are not immune to SCC. SCC of certain nickel alloys has occurred in high-temperature halogen ion environments, high-temperature waters, and high-temperature alkaline systems and environments containing acids and H_2S . SCC is dependent on the stress level, chloride concentration, alloy composition, and temperature. Susceptible temperature ranges vary from 175-330 °C. Higher temperatures will tend to lower the chloride threshold concentration and stress levels required for cracking. Ferritic stainless steels are usually not considered susceptible to SCC. Stressed martensitic stainless steel grades can crack in chloride environments.

CONCLUSIONS

Compliance with environmental regulations has required design of a waste management system to safely treat and reduce the volume of solid shipboard waste for the U.S. Navy. The U.S. Navy in cooperation with industry has developed conceptual designs for a plasma arc waste destruction system (PAWDS) capable of meeting strict shipboard weight, size and operational criteria.

A hotwall design considered a refractory lined chamber to process shipboard waste. Silicon carbide, high purity alumina, and alumina-chromia working refractories were considered the best candidates for the hotwall PAWDS design. Weight and size limitations, maintainability, and reliability of the hotwall design led to the consideration of alternative PAWDS designs.

The final candidate material in the coldwall PAWDS will not be the most corrosion-resistant alloy in all possible environments. The protective chromia, alumina, and silica oxides scales formed on the alloys have different growth kinetics, mechanical properties, and corrosion resistances to oxidizing and reducing atmospheres, sulfidation, chloridation, hot corrosion, dewpoint corrosion, galvanic attack, hydrogen interactions, and environmental assisted cracking. The alloys also have different long-term mechanical properties at high temperatures.

For the water-cooled coldwall design with temperatures below 600 °C, alloy UNS N06022 would provide optimum resistance to corrosion processes possible in the PAWDS. Similar alloys that could provide possible service are: UNS N10276, UNS N06455, and UNS N06059. These are resistant to pit initiation due to a high level of molybdenum present in the alloys. For adequate to good resistance, alloy UNS N06625 is recommended. It does not have as high a resistance to pit initiation as UNS N06022, but has better high-temperature strength which may prove acceptable in a coldwall environment. None of the alloys recommended have a long-term (creep) stress rupture strength existing over 3 ksi. The chamber wall will have to be thick enough to compensate for this lack of high-temperature strength. The alloys considered thermally degrade with time at temperatures above 600 °C.

For an air-cooled or water-cooled chamber where the temperature is around 1000 °C, alloy UNS R30556 is recommended to provide the best service for a combination of oxidation, carburization, chloridation, and hot corrosion resistance. Alloy UNS N08120 may also provide adequate service in the air-cooled environment. These alloys maintain good high-temperature strength up to 900 °C, but the long-term high-temperature stability of these alloys still needs to be established. Two other alloys, UNS N06230 and UNS N07041, have better high-temperature strength and resistance to long-term thermal degradation of the alloy microstructure, but their resistance to hot corrosion, sulfidation and chloride-containing salts is not known at this time. The selection of fabricating processes must be chosen carefully for nickel-based superalloys. Liquid metal embrittlement can occur when brazing precipitation-strengthened alloys such as UNS N07041. Many nickel superalloys crack when subjected to tensile stresses in the presence of some molten filler metals.

Testing is strongly recommended in high-temperature environments that properly simulate the conditions in the PAWDS - particularly, environments that simulate the abrasive conditions, corrodents, and the temperature fluctuations generated by the plasma arc torch on the candidate test alloys. Alloys need to be tested in a simulated PAWDS environment and under similar operating conditions envisioned for the eventual shipboard PAWDS. High temperature erosion testing of several candidate materials is presently being planned.

REFERENCES

- 1 - R.L. Jones, *High Temperature Technology*, v. 6 187 (1988).
- 2 - Handbook of Refractory Practice, 1st ed., Harbison-Walker/Indresco Inc, Pittsburgh, PA, PR-12 (1992).
- 3 - L.M. Sheppard, "Corrosion Resistant Ceramics for Severe Environments", *Ceramic Bulletin*, v.70, 1146 (1991).
- 4 - H.E. Wolfe, P.A. Beaulieu, "Update on Refractories for Hazardous Waste Incineration", *Corrosion/89*, paper 551, NACE International, Houston, TX (1989).
- 5 - *Ceramic Industry*, v. 154, 114 (1996).
- 6 - D.P. Butt, R.E. Tressler, K.E. Spear, "Corrosion of Silicon Carbide Materials in Metallurgical Heat-Treatment Environments", *American Ceramic Society Bulletin*, v. 71, 1683 (1992).
- 7 - S. Manning-Meier, D.N. Nissley, K.D. Sheffler, "Status of Ceramic Thermal Barrier Coatings - Gas Turbine Application and Life Prediction Methods", Proceedings of the 1990 Coatings for Advanced Heat Engines Workshop, Catine, ME, U.S. Department of Energy, II-57 (1990).
- 8 - R.A. Miller, C.E. Lowell, "Failure Mechanisms of Thermal Barrier Coatings Exposed to Elevated Temperatures", *Thin Solid Films*, v. 95, 265 (1982).
- 9 - S.M. Meier, D.N. Nissley, K.D. Sheffler, "Thermal Barrier Coating Life Prediction Model Development", NASA Contractor Report 189111, NASA Lewis Research Center, Cleveland, OH (July 1991).
- 10 - I. Nettleship, R.Stevens, *International J. High Technology Ceramics*, v. 3, 1 (1987).
- 11 - S.C. Singhal, R.J. Bratton, *Trans. ASME - J. Engineering for Power*, v.102, 770 (1980).
- 12 - R.L. Jones, "The Development of Hot Corrosion Resistant Zirconia Thermal Barrier Coatings", Proceedings of the 1990 Coatings for Advanced Heat Engines Workshop, Catine, ME, U.S. Department of Energy, II-67 (1990).
- 13 - R.L. Jones, "Experiences in Seeking Stabilizers for Zirconia Having Hot Corrosion Resistance and High Temperature Tetragonal Stability", NRL/MR/617--96-7841 (April, 1996).
- 14 - Materials of Construction for Shipboard Waste Incinerators, National Research Council, National Academy of Sciences, Washington, DC, 91-92 (1977).
- 15 - P. Elliot, "Practical Guide to High-Temperature Alloys", *Materials Performance*, v. 28, 57 (1989)
- 16 - F.H. Stott, G.C. Wood, J. Stringer, "Influence of Alloying Elements on the Development and Maintenance of Protective Scales", *Oxidation of Metals*, v. 44, 113 (1995).
- 17 - M. Shütze, "Mechanical Properties of Oxide Scales", *Oxidation of Metals*, v.44, 29 (1995).
- 18 - Corrosion, 2nd ed, L.L. Sheir, ed., Newes-Butterworths, London, 7:101 (1976).

- 19 - W.B. Hoyt, R.H. Caughey, "High Temperature Metal Deterioration in Atmospheres Containing Carbon-Monoxide and Hydrogen", *Corrosion*, v.15, 627t (1959).
- 20 - P.A. Lefrancois, W.B. Hoyt, "Chemical Thermodynamics of High Temperature Reactions in Metal Dusting Corrosion", *Corrosion*, v.19, 360t (1963).
- 21 - G.Y. Lai, *Proceedings in High Temperature Corrosion of Energy Systems*, M.F. Rutman, ed., The Metallurgical Society, 45 (1980).
- 22 - S. Mrowec, "The Problem of Sulfur in High-Temperature Corrosion", *Oxidation of Metals*, v. 44, 177 (1995).
- 23 - *Corrosion*, 2nd ed, L.L. Sheir, ed., Newnes-Butterworths, London, 7:90 (1976).
- 24 - *ibid.* 7:93.
- 25 - P. Ganesan, G.D. Smith, L.E. Shoemaker, "The Effects of Exclusions of Oxygen and Water Vapor Contents on Nickel-Containing Alloy Performance in a Waste Incineration Environment", *Corrosion/91*, paper 248, NACE International, Houston TX (1991).
- 26 - H.H. Krause, *J. Materials for Energy Systems*, v.7, 322 (1986)
- 27 - Metals Handbook, *Corrosion*, v.13, 10th ed., ASM International, Materials Park, OH, 997 (1987).
- 28 - G.D. Smith, P. Ganesan, L.E. Shoemaker, The Effect of Environmental Excursions within the Waste Incinerator on Nickel-Containing Alloy Performance, *Corrosion/90*, paper 280, NACE International, Houston TX (1990).
- 29 - C.T. Wall, J.T. Groves, E.J. Roberts, "How to Burn Salty Sludges", *Chemical Engineering*, v. 7 (April 14, 1975).
- 30 - P. Ganesan, G.D. Smith, L.E. Shoemaker, "The Effects of Excursions of Oxygen and Water Vapor on Nickel Containing Alloy Performance in a Waste Incineration Environment", *Corrosion/91*, paper 248, NACE International, Houston TX (1991).
- 31 - J.F. Wilkes, D.A. Shifler, "Historical Perspectives of Intergranular Corrosion of Boiler Metal by Water", *Corrosion/93*, paper 44, NACE International, Houston, TX (1993).
- 32 - K.T. Chiang, F.S. Pettit, G.H. Meier, "Low Temperature Corrosion", in *High Temperature Corrosion*, NACE-6, R.A. Rapp, ed., NACE International, Houston, TX, 519 (1983).
- 33 - W. T. Reid, *External Corrosion and Deposits - Boiler and Gas Turbines*, Fuel and Energy Science Series, J.M. Beer, ed., American Elsevier, New York, 104 (1971).
- 34 - G. Wacker, W.L. Wheatfall, "Corrosion Problems Associated with Shipboard Waste Incineration Systems", 1976 Triservice Corrosion Conference, Philadelphia, PA, 185, October, 26-28, 1976.
- 35 - P. Elliott, "Materials Performance in High-Temperature Waste Combustion Systems", *Materials Performance*, v.32, 82 (1993).
- 36 - H.H. Krause, D.A. Vaughn, P.D. Miller, "Corrosion and Deposits from Combustion of Solid Waste", *Trans. ASME - J. Engineering Power*, v.95, 45 (1973).
- 37 - R.M. Davison, T. Debold, M.J. Johnson, "Corrosion of Stainless Steels", *Corrosion*, v.13, 10th ed., ASM International, Materials Park, OH, 559 (1987).

- 38 - R.A. Smith, S.R. I. Saunders, Corrosion, 3rd ed., L.L. Sheir, R.A. Jarman, G.T. Burstein, Butterworth-Heinemann, London, 7:136 (1994).
- 39 - M.H. Kamdur, "Liquid Metal Embrittlement" , Corrosion, v.13, 10th ed., ASM International, Materials Park, OH, 171 (1987).
- 40 - M.G. Fontana, N.D. Greene, Corrosion Engineering, 2nd ed., McGraw-Hill, New York, 294 (1978)
- 41 - Superalloys- A Technical Guide, E.F. Bradley, ed., ASM International, Materials Park, OH (1988).
- 42 - Alloy and Microstructural Design, J.K. Tien, G.S. Ansell, eds., Academic Press, New York (1976).
- 43 - J.K. Tien, S. Purushothaman, "The Metallurgy of High Temperature Alloys", in Proceedings: Properties of High Temperature Alloys - with Emphasis on Environmental Effects, v. 77-1, Z.A. Foroulis, F.S. Pettit, eds., The Electrochemical Society, Pennington, NJ, 3 (1976).
- 44 - Metals Handbook, Properties and Selection: Irons, Steels, and High-Performance Alloys, 10th ed. v.1, 626-7, ASM International, Materials Park, OH (1990).
- 45 - Metals Handbook, Properties and Selection: Stainless Steels, Tool Materials, and Special-Purpose Metals, 9th ed. v.3 , 144, ASM International, Materials Park, OH (1980).
- 46 - F.S. Pettit, J.K. Tien, "Hot Gas Environment - Alloy Reactions and Their Relation to Fatigue", Corrosion Fatigue: Chemistry, Mechanic, and Microstructure, NACE 2, NACE International, Houston, TX, 576 (1972).
- 47 - Alloy Data, Carpenter Technology Corporation, Carpenter Steel Division.
- 48 - High Temperature Product Literature and Hastelloy Corrosion-Resistant Alloy Product Literature, Haynes International, Kokomo, IN, 1991-1996.
- 49 - Product Information, The Carborundum Company, Refractories Division

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